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Short communication

Comparative voltammetric behaviour of H- and O-atoms on a Pt electrode in sulphuric acid solutions within the 293 K to 233 K range

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The influence of temperature in electrochemical reactions was considered with special attention some decades ago [1–13] and investigated in even more detail in recent years [14–20]. The effect of temperature upon the double layer capacitance at electrode/electrolyte interfaces [5,8,12,20] contributes to a better understanding of the structure of the electrical double layer and its influence on the kinetics of the electrode reactions. One of the earliest studies was focussed on the hydrogen evolution reaction (HER) on Hg to study comparatively the mechanism of the reaction in acid electrolytes on liquid and solid mercury [21]. Most recent studies were devoted to the HER in perchloric acid solutions on platinum. The kinetics of this reaction were studied from room temperature to 120 K, using slow potential sweep rate voltammetry with $HClO_4 \cdot 5.5\ H_2O$ electrolyte [18], and were interpreted through the Volmer–Tafel mechanism.

At this stage, it seems particularly interesting to investigate the H-atom electroadsorption/electrodesorption on platinum in acid solution as one of the simplest electrochemical reactions at solid electrodes. This reaction, as well as the early stages of O-atom electroadsorption/electrodesorption, are of utmost importance in fundamental electrochemistry. Both reactions were studied extensively in recent years, mostly at room temperature, to inspect particularly the influence of the crystalline metal faces, the electrolyte composition, and the electrode treatment [22–25].

The present work reports the voltammetric behaviour of H- and O-adatoms on different platinum electrodes in 1 *M* H_2SO_4 covering the temperature range 293 to 233 K. It is thus possible to extend the low temperature investigations of the electrochemical reactions by working at temperatures far below the freezing point of the electrolyte, which is at 268 K.

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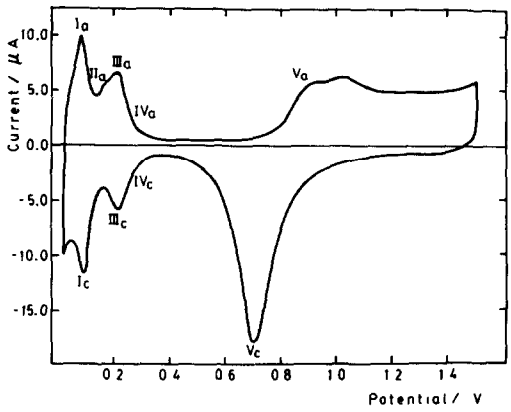

Fig. 1. Voltammogram of Pt(pc) run at 0.1 V/s in 1 *M* H_2SO_4 at 293 K.

The experimental setup consisted of a conventional electrolysis cell with three electrodes. The working electrodes were polyfacetted platinum single crystal spheres prepared following a slightly modified version of the melting procedure described earlier in the literature [26,27]. A Pd/H_2 reference electrode ending with a Luggin–Haber capillary tip [28] and a Pt cylindrical counterelectrode (3 mm radius), surrounding the working electrode, were used. The working electrode and the tip of the Luggin were placed on the axis of the Pt cylinder and separated by a 1 mm gap. Two types of working electrodes were used, namely, polyfacetted platinum, Pt(pc) and preferred crystalline oriented platinum, Pt(pco). The latter was obtained by using the electrochemical facetting technique already described elsewhere [29–31]. In the text, potential values are referred to the RHE scale temperature after correction by using the temperature coefficient taken from the literature [28]. The temperature was monitored by two precision thermistors (YSI 44001A), one of which was placed in the bulk of the solution while the other was adjacent to the working electrode surface, avoiding as much as possible shielding effects.

The voltammetric runs were made at 293 K by using a conventional circuitry operating at 0.100 V/s and covering a constant potential window comprised between $E_l = 0.015$ V and $E_u = 1.480$ V, which is the potential range where both H- and O-atom electroadsorption/electrodesorption reactions take place. Voltammetric results are depicted in Figs. 1–5.

The voltammogram of Pt(pc) run at 293 K in 1 *M* H_2SO_4 (Fig. 1), which is included for the sake of comparison, shows the typical H-adatom electroadsorption/electrodesorption peaks I_a/I_c, II_a, III_a/III_c and IV_a/IV_c, in the 0 to 0.4 V range, and the O-atom electroadsorption/electrodesorption contribution, V_a/V_c, in the 0.5 V to 1.4 V range or thereabouts. The same run made at 233 K exhibits a voltammogram for the H-adatom reaction without the appearance of peak II_a, an increasing contribution of peaks IV_a/IV_c and a remarkable decrease in the charge of peaks V_a/V_c.

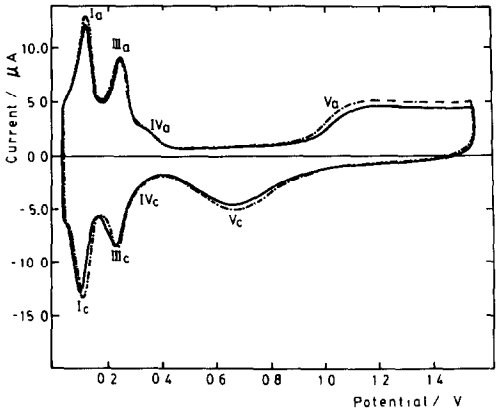

Fig. 2. Voltammogram of Pt(pc) run at 0.1 V/s in 1 *M* H_2SO_4 at 233 K (liquid phase 3.2 *M* H_2SO_4). (———) Voltammogram run between 0.015 V and 1.480 V; (·–·–·) voltammogram after 30 min RSWPS treatment ($E_u = 1.480$ V, $E_l = 0.015$ V, $f = 6$ kHz)

Another experiment was made in order to attempt to produce electrochemical facetting of the platinum below 268 K. For this purpose, the Pt(pc) electrode, kept at 233 K, was subjected to a repetitive square wave potential signal (RSWPS) between upper ($E_u = 1.480$ V), and lower ($E_l = 0.015$ V) potential limits at a frequency (f) of 6 kHz, for a time (t) equal to 30 min [30–32]. In this case, one can observe throughout the voltammogram run immediately afterwards, without removing the electrode from the solution, that no appreciable electrochemical facetting can be observed voltammetrically (Fig. 2). Conversely, interesting changes can be obtained voltammetrically by carrying out the experiment in the following way. Firstly, the electrochemical facetting was accomplished at 293 K, and subsequently the temperature was decreased to 233 K. The voltammetric response of the treated electrode exhibits no appreciable changes in the charges for both H- and O-adatom electrochemical reactions (Fig. 3), but in contrast, there is a remarkable increase in the heights of peaks III_a/III_c which are related to strongly bound H-adatom reactions. This occurs at the expense of a decrease in the heights of peaks I_a/I_c associated with weakly bound H-adatom reactions. Furthermore, the relative contributions of peaks IV_a/IV_c are enhanced as compared to the blank, and also slight voltammetric changes can be observed in the O-adatom potential range. Now, when at this stage the temperature is decreased to 233 K, that is, below the freezing point of the electrolyte, the voltammogram resulting at this temperature becomes considerably different from those described above. In this case, one can observe a remarkable increase in the H-adatom charge, which is estimated to be about 50% greater than that found for the blank. In addition a new small peak at nearly 0 V emerges (I'_a). This new peak cannot be attributed to diffusion controlled molecular hydrogen electrooxidation because of the symmetry in charge and shape of the voltammogram, and the shift of hydrogen evolution towards more negative potentials as the temperature is decreased, which makes the amount of molecular

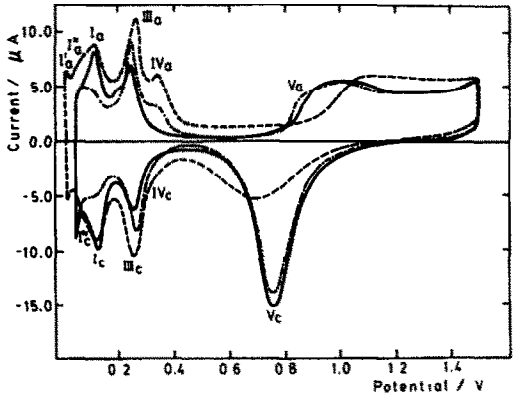

Fig. 3. Voltammogram of Pt run at 0.1 V/s in 1 *M* H_2SO_4. (———) Voltammogram of Pt(pc) run between 0.015 V and 1.480 V at 293 K; (·–·–·) voltammogram after 30 min RSWPS treatment ($E_u = 1.480$ V, $E_l = 0.015$ V, $f = 6$ kHz), at 293 K; (— — —) voltammogram of Pt(pco) at 233 K (liquid phase 3.2 *M* H_2SO_4).

hydrogen accumulated much smaller at 233 K than at 293 K, is in agreement with recently reported data [18]. Under these conditions, peaks I_a/I_c become wider (shoulders I_a''/I_c'', respectively) and their relative contributions increase as compared to those recorded for Pt(pco). Furthermore, peak II_a is no longer observed and the contributions of peaks IV_a/IV_c become more relevant than in the voltammograms run previously. Finally, the O-adatom electrochemical reactions are slowed down significantly, both in charge and rate. However, if the same experiment is continued by subsequently raising the temperature of the system to 293 K, the voltammogram resulting at this temperature shows that the H-adatom voltammetric charge has returned to nearly the same value found initially for Pt(pco), yet the

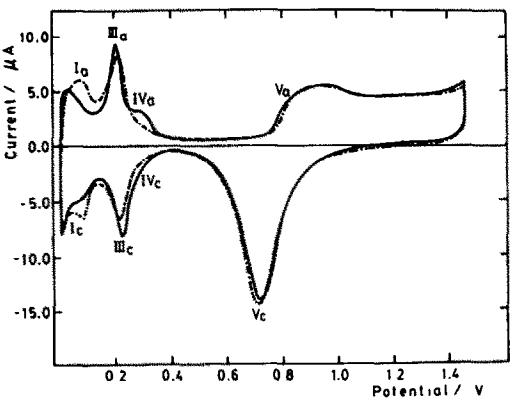

Fig. 4. Voltammogram of Pt run at 0.1 V/s in 1 *M* H_2SO_4. (———) Voltammogram of Pt(pco) at 293 K; (·–·–·) voltammogram of Pt(pco) after raising the temperature from 233 K (liquid phase 3.2 *M* H_2SO_4) to 293 K.

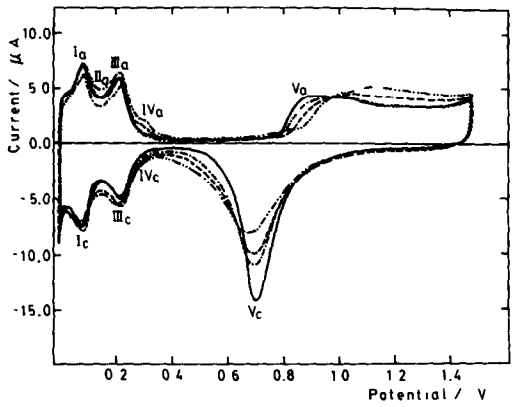

Fig. 5. Voltammogram of Pt(pc) run at 0.1 V/s in 1 *M* H_2SO_4. (———) At 293 K; (·–·–·) 269 K; (— — —) 252 K (liquid phase 2.3 *M* H_2SO_4); (··–··–··) 240 K (liquid phase 2.8 *M* H_2SO_4).

distribution of the voltammetric peaks is rather different (Fig. 4). Apparently, the entire voltammogram shows a trend to approach the distribution of peaks already described for Pt(pc). These results are particularly interesting because they give a first indication that the surface of Pt(pco) could be modified through only a few low frequency potential scans, at a temperature lower than the freezing point of the electrolyte.

The gradual changes in the voltammograms of Pt(pc) in 1 *M* H_2SO_4 in going from 293 to 240 K are depicted in Fig. 5. This behaviour depends also to some extent on the initial concentration and nature of the electrolyte, as has been concluded from previous work with liquid electrolyte solutions [25].

It should be noted that according to the $H_2SO_4 + H_2O$ phase diagram [33], the cooling of 1 *M* H_2SO_4 below its freezing point results in a phase separation of ice and liquid sulphuric acid with a temperature dependent concentration. The eutectic $H_2O + H_2SO_4 \cdot 6\ H_2O$ freezes at 211 K. Therefore, a decrease in temperature below 268 K produces a solid (ice)/liquid (x *M* H_2SO_4) system with x ranging from 1 to nearly 5 as the temperature decreases from 268 to 211 K. Thus, for all conditions described in this paper, liquid sulphuric acid is the conductive phase. Incidentally, in the temperature range of the experiments the electrical conductance of the liquid phase increases by a factor of about 3 [34]. Therefore, as far as the electrical resistance of the system is concerned, it will tend to behave either rather constant or change rather slightly because the decrease in the volume of the liquid phase is counterbalanced by the increase in electrical conductance. Hence, the influence of the temperature on the electrochemical results, except in the O-adatom electrosorption potential range, cannot be ascribed specifically and predominantly to a concentration change in the conducting phase.

The results of these experiments can be summarized as follows.

(i) The temperature dependences of the H- and O-atom electroadsorption/electrodesorption reactions on platinum in 1 *M* H_2SO_4 are considerably different.

The reactions involving H-adatoms appear to be nearly temperature independent in the range investigated, whereas those comprising O-adatoms depend strongly on the temperature. This fact is consistent with the participation of a significant proton tunnelling in the reactions involving H-atoms [35].

(ii) The potentials of the H-adatom electroadsorption/electrodesorption reactions referred to the RHE in the same solution at the same temperature remain practically constant in the entire temperature range covered by the present work. Conversely, the threshold potential for O-electroadsorption shifts positively as the temperature decreases. This means that for a constant upper switching potential, the O-electroadsorption charge decreases as the temperature decreases. This fact is obviously reflected in the O-electrodesorption reaction and it should be related largely to the change in the concentration of the liquid sulphuric acid phase [36].

(iii) The H-adatom charge at low temperature attains a limiting value, which apparently exceeds slightly that established as the H-adatom monolayer charge at room temperature (0.210 mC/cm^2 for Pt(pc)). This intriguing result cannot be explained exclusively through a change in the roughness factor because the charge difference appears only at low temperature and disappears reversibly on raising the temperature. Although this effect certainly has to be explored more exhaustively before a definite interpretation can be advanced, it could be related to a greater accessibility of the H-atoms to the electrode, resulting from the change in the structure of the electrolyte or produced by a transient metal surface reconstruction.

(iv) At low temperature, the new H-electrooxidation peak (I'_a) observed at nearly 0 V, is most likely related directly to the proper HER. This peak could be associated with the new kind of intermediate for the HER which has been postulated recently from surface infrared spectroscopy measurements [37,38].

(v) Repetitive voltammetric measurements, made as the temperature is decreased from 298 K to temperatures below the freezing point of the solution, have shown that at the liquid–solid phase transition there is a temporary current discontinuity. This very reproducible phenomenon, which can be observed by producing a very carefully controlled and slow temperature change, depends on the electrolyte concentration. Neither before, nor after the solid–liquid phase transition, could erratic currents in the voltammetric potential window be observed as found for the HER potential range [19]. The current discontinuity could be associated with a local resistance due to the specific type of order attained during the phase transition.

(vi) The H-adatom electroadsorption/electrodesorption for Pt(pc) scanned between 0.005 V and 0.450 V, in the cooled electrolyte, remains unaltered after very prolonged potential cycling. It is known that voltammetry in that potential range is extremely sensitive to traces of organic impurities and to the slowness of anion adsorption. It appears that these drawbacks usually found in voltammetric measurements with Pt/liquid state electrolyte solutions tend to smooth over considerably in cooled solutions.

(vii) Finally, when Pt(pco) electrodes are employed, surface restructuring using low frequency voltammetry becomes possible even below the freezing point of the solution but, in contrast, electrochemical facetting could not be achieved at the

frequency of 6 kHz. It is known that the metal surface plays a dynamic role in the interaction with H-adatoms, but this dynamic behaviour is associated with the perturbing potential frequency [25]. Apparently, when the latter is lower than the relaxation time of the H_2O molecule at the interface, no restructuring can be produced. If one admits that the possible structure of water at the inner Helmholtz layer would be comparable to that of ice I, which exists in the 249.6 to 243 K range, then the corresponding relaxation time would be close to 0.168 ms [39,40]. On the other hand, for lower frequencies of the periodic perturbing potential, the voltammetric behaviour of Pt(pco) can be changed to close to that of Pt(pc). These results agree with the non-stationary voltammetric behaviour of recently prepared Pt(pco) upon cycling under different conditions [41].

In conclusion, these preliminary results, particularly those concerning the H-atom electroadsorption/electrodesorption reaction, show some intriguing new effects which certainly deserve further investigation. They seem particularly attractive for many areas which are of primary importance in electrochemistry.

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